



Ultrasound-assisted production of biodiesel and ethanol from spent coffee grounds



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HIGHLIGHTS

- Use of spent coffee grounds as source for production of biodiesel and ethanol.
- Study of the ultrasound-assisted extraction of spent coffee grounds oil.
- Biodiesel production by ultrasound-assisted esterification reaction.
- Study of the hydrolysis of the oil free spent coffee ground.
- Ethanol production by *Saccharomyces cerevisiae* using the hydrolysate.

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ABSTRACT

This study evaluates the production of biodiesel and ethanol from spent coffee grounds (SCG). The extraction of oil from SCG, biodiesel production and ethanol production processes were studied. The liquid-to-solid ratio and temperature were evaluated in the ultrasound-assisted extraction of the oil from SCG. The highest yield (12%) was obtained using 4 mL g⁻¹ liquid-to-solid ratio at 60 °C for 45 min. The process to produce biodiesel showed a yield of 97% into fatty acid methyl esters (FAME). The highest glucose yield (192 mg g_{SCG}⁻¹) was obtained by hydrolysis with 0.4 mol L⁻¹ sulfuric acid at 121 °C for 15 min. The hydrolysate was used as fermentation medium for ethanol production by *Saccharomyces cerevisiae* obtaining 19.0 g L⁻¹ at 10 h of process of ethanol with a yield of ethanol and productivity of 0.50 g g⁻¹ and 1.90 g L⁻¹ h⁻¹, respectively. Spent coffee grounds were considered a potential feedstock for biodiesel and ethanol production.

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1. Introduction

Global demand for energy has increased continuously since the industrial revolution and it is still increasing fast given current industrial development and population growth. About 80% of the world energy consumption is supplied by fossil fuels, which are non-renewable and one day will be exhausted (International Energy Agency, 2013). Pressure to replace fossil fuels exists and renewable energy sources are being studied and have been implemented in large scale to cope with this increasing demand

(Al-Hamamre et al., 2012; Correia et al., 2013; Rocha et al., 2011; Song et al., 2008). Among these renewable energy sources, second generation ethanol and biodiesel have been recognized as feasible energy sources given its compatibility with the current combustion engine technologies and existing distribution networks (Cheng et al., 2008; Rocha et al., 2014).

The concept of bio-refineries has been proposed as an option to increase the sustainability of transportation fuels derived from renewable sources (Kwon et al., 2013). The use of raw materials that can produce both ethanol and biodiesel in a single industry is the desire of integrated bio-refineries. The conversion of different biomass into biodiesel, ethanol or other biofuels increases the flexibility and gives the possibility of diversifying the feedstock for better supply security and cost stability of these plants (Al-Hamamre et al., 2012).

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Spent coffee grounds have potential to become a raw material for integrated bio-refineries. This residue produced after brewing coffee grounds contain oil that can be extracted and converted into biodiesel (Abdullah and Koc, 2013; Kondamudi et al., 2008; Oliveira et al., 2008) and cellulosic material that can be converted into ethanol (Kwon et al., 2013).

Coffee figures as one of the world's largest agriculture products and it is used mainly for beverage. According to the Food and Agriculture Organization (FAO), the world's coffee production was 8.8 million tons in 2012, been Brazil, Vietnam, Indonesia and Colombia the main producing countries (FAOSTAT, 2013). Although much of the ground coffee is consumed in homes, bars and restaurants, large facilities that processes coffee bean to produce soluble coffee can provide a large amount of spend coffee ground to bio-refineries.

The oil content in coffee ranges in mass fraction from 11% to 20% depending on its type. Arabica variety (*Coffea arabica*) contains between 12% and 18% of oil, while the robusta variety (*Coffea canephora*) contains about 9–14% of oil (Al-Hamamre et al., 2012; Oliveira et al., 2008; Abdullah and Koc, 2013). Biodiesel production from coffee oil involves collection and transportation of coffee residue, drying, extraction of the oil and biodiesel production (Abdullah and Koc, 2013).

Several processes have been proposed for the extraction of oil from coffee grounds, such as Soxhlet oil extraction and supercritical oil extraction. Soxhlet oil extractions are very time consuming requires a large amount of solvent and energy and has low productivity (Al-Hamamre et al., 2012; Araújo and Sandi, 2007). Supercritical carbon dioxide extraction requires high pressure, high temperature and coffee grounds with very low water content (Couto et al., 2009). Ultrasound-assisted solvent extraction has been applied with success in the extraction of soybean and microalgae oil (Araujo et al., 2013; Li et al., 2004; Rodrigues and Fernandes, 2009). It showed to enhance the extraction of oil from materials with low or high moisture contents at a low energy cost.

The residue obtained after the extraction of the oil can be used as source for ethanol production. Several steps can be required to convert SCG (or any waste material) into ethanol: pretreatment, enzymatic hydrolysis and fermentation (Correia et al., 2013; Rocha et al., 2014; Saha and Cotta, 2010). The pretreatment step aims to disrupt the recalcitrant structures of the material increasing its digestibility prior to enzymatic hydrolysis, which releases sugars from the organic matrix. Conversion of the sugars into ethanol is then carried out through fermentation (Rocha et al., 2011).

This work evaluates the production of biodiesel and ethanol from spent coffee grounds. Ultrasound-assisted solvent extraction from waste coffee grounds was studied and optimized. Biodiesel was produced through saponification of the oil followed by acid hydrolysis and esterification with methanol to obtain biodiesel. The oil-free spent coffee ground was used to produce ethanol using *Saccharomyces cerevisiae*.

2. Methods

2.1. Spent coffee grounds

Spent coffee grounds (SCG) were obtained from a local coffee shop (Fortaleza, Ceará, Brazil) that uses Arabica coffee grounds. The SCG were dried in an oven at 105 °C for 24 h to reduce its water content to the mass fraction of 3%. Drying aimed to avoid spoilage of the SCG and to avoid the growth of microorganisms.

2.2. Ultrasound-assisted oil extraction

The spent coffee grounds were placed inside a paper *sachet* and immersed in hexane inside a 500 mL hermetically sealed beaker.

Sonication was carried out for 45 min at 40 kHz and temperatures ranging from 20 °C to 60 °C. A 2.7 L ultrasonic bath (UltraCleaner 1450A, Unique, Brazil), delivering 160 W to the bath, was used in the experiments. After the extraction, the *sachet* containing the SCG was removed and the mixture containing the oil was transferred to a rotary evaporator to remove hexane under moderate vacuum. The oil was transferred to an oven drier set at 104 °C and kept there for 6 h to remove any hexane that might have remained in the oil.

A 2² factorial experimental design was carried out to evaluate how the solvent to SCG ratio (mL g⁻¹) and the temperature influences the amount of oil extracted from the SCG. In the study, the solvent to SCG ratio ranged from 2 mL g⁻¹ to 4 mL g⁻¹ and the temperature ranged from 20 °C to 60 °C (Table 1). These ranges were based on common ranges used in the literature for oil extraction. The data were analyzed using the software Statistic v7.0 (Statsoft Inc., USA) via multiple regression analysis using the least squares method, taking into account the isolated terms and interaction of the studied variables.

The oil was characterized by determining its acid value, density and fatty acid composition. Acid index (AI) was determined using the AOCS Ca 5a-40 method (AOCS, 2013). Density was directly measured using a digital density meter (Anton Parr model DMA 500, Graz, Austria).

The oil composition expressed as fatty acids content was determined using the AOCS Ce 2-66 method (AOCS, 2013). The oil was methylated and analyzed in a gas chromatograph (Thermos Ultra) with an FID detector. A capillary column BPX5 SGE (30 m × 0.25 mm × 0.25 μm) was used to separate the fatty acid methyl esters. The injector and detector temperature was set to 250 °C and the column temperature was programmed to increase from 110 °C to 215 °C (at rate of 5 °C min⁻¹) remaining at 215 °C for 24 min.

2.3. Biodiesel production

The oil was placed in a 500 mL round bottom flask and mixed with an alcoholic solution of KOH (30 g L⁻¹). The mixture sonicated for 30 min in an ultrasonic bath (40 kHz, 160 W) operating at ambient temperature. After the saponification reaction, the mixture was acidified with a H₂SO₄ solution (volumetric fraction of 27%) and transferred to a separating funnel. The aqueous layer was discarded and the supernatant containing the free fatty acids was heated at 110 °C until total dehumidification.

The esterification reaction was also carried out in an ultrasonic bath (40 kHz, 160 W). Free fatty acids, methanol (methanol/fatty acid molar ratio of 9:1) and H₂SO₄ (3.5%) were added to a 500 mL round bottom flask and sonicated for 60 min at 60 °C. These conditions were based on previous studies on the optimization of free fatty acids sono-esterification process (Lima et al., 2012; Santos et al., 2009, 2010). After esterification, the biodiesel was placed in a separating funnel and washed three times with water at 25 °C to remove impurities, methanol and H₂SO₄. Finally, the biodiesel was heated at 110 °C until total dehumidification. Gas chromatography was also used to characterize the biodiesel. The conditions used in the assays were the same as described for the oil characterization.

2.4. Ethanol production

The production of ethanol was carried out in two steps: hydrolysis of the oil-free spend coffee ground followed by fermentation.

The oil-free spent coffee grounds were hydrolyzed with diluted sulfuric acid. Different concentrations of H₂SO₄ (0.4 mol L⁻¹ and 0.8 mol L⁻¹) were applied and studied to evaluate its performance. The oil-free SCG and H₂SO₄ solution were mixed as to form a slurry with a solid concentration of 20%. The slurry was homogenized for 5 min to ensure that the solids were dispersed uniformly. The

Table 1
Yield of oil obtained by ultrasound-assisted extraction of spent coffee grounds.

Experiment	Liquid-to-solid ratio (solvent/SCG, mL g ⁻¹)	Temperature (°C)	Yield (% g _{oil} /g _{SCG})
1	2	20	3 ± 1
2	4	20	9 ± 1
3	2	60	3 ± 1
4	4	60	12 ± 1
5	3	40	7 ± 1
6	3	40	6 ± 1
7	3	40	7 ± 1

hydrolysis was carried out in an autoclave for 15 min at 121 °C. After hydrolysis, the solid fraction was separated from the liquid through vacuum filtration (GAST Manufacturing model DOA-P704, Michigan, USA). The pH of the liquid fraction was adjusted to 5.0 ± 0.3 with a NaOH solution (1 mol L⁻¹) and the amount of glucose, xyloarabin (xylose plus and arabinose), 5-hydroxymethyl-2-furfural, furfural, lactic acid and acetic acid were analyzed. All experiments were conducted in triplicate. A treatment carried out without adding sulfuric acid was used as a control.

The fermentations were carried out using pure *S. cerevisiae* culture that was isolated from a commercial yeast Saf-momento (SAF Argentina, Buenos Aires). The inoculum was initially activated in Agar Sabouraud Biolife medium (5.0 g L⁻¹ peptone; 15.0 g L⁻¹ glucose and 15.0 g L⁻¹ Agar) and incubated at 30 °C for 48 h. Then the culture was transferred to a 250 mL Erlenmeyer containing 200 mL of medium: 30 g L⁻¹ glucose, 5.0 g L⁻¹ yeast extract, 10 g L⁻¹ (NH₄)₂SO₄, 4.5 g L⁻¹ KH₂PO₄, 1.0 g L⁻¹ MgSO₄·7H₂O and 0.65 g L⁻¹ ZnSO₄. The pH was adjusted to 5.5 with 1 mol L⁻¹ NaOH or 1 mol L⁻¹ HCl and sterilized at 110 °C for 10 min. The culture was maintained at 30 °C for 24 h and centrifuged at 10,000g for 10 min to obtain the initial biomass for the fermentation assays.

The ethanol production was carried out in 250 mL Erlenmeyer containing 50 mL of the hydrolysis product and was done in a rotary shaker TE240 (Tecnal – Piracicaba, Brazil) at 30 °C and 150 rpm. The initial concentration of inoculated microorganism was 10 g L⁻¹. Samples were collected at predetermined times and centrifuged (BioEng Centrifuge model SER-6000, Piracicaba, SP – Brazil) at 10,000g for 10 min. The supernatant was used to analyze the amount of glucose, xyloarabin and ethanol. All experiments were conducted in triplicate.

The concentration of glucose, arabinose, xyloarabin and ethanol was measured using High Performance of Liquid Chromatography – HPLC (Milford, MA, USA) equipped with refractive index detector Waters 2414 and Supelcogel C-610H 7.8 × 300 mm column, mobile phase: H₃PO₄ 0.1%, flow rate: 0.5 mL min⁻¹ at 30 °C and injection volume: 10 µL (Pinheiro et al., 2008).

The fermentation inhibitors: acetic acid, lactic acid, 5-hydroxymethyl-2-furfural (HMF) and furfural were analyzed using an HPLC working at 65 °C with Aminex HPX-87H column, H₂SO₄ 5 mmol L⁻¹ as eluent at a flow rate 0.5 mL min⁻¹ (Rocha et al., 2014).

2.5. Statistical analysis

Statistical analysis was carried out by one-way analysis of variance (ANOVA) at a significance level of 95% using the software Statistica v7.0. The data were also analyzed by Tukey test using the software Microcal Origin v8.1 at a significance level of 95%.

3. Results and discussions

3.1. Oil extraction

Table 1 shows the amount of oil extracted from SCG at different liquid-to-solid ratio (solvent/SCG) and temperatures. The yields

ranged from 3% to 12% on a dry weight basis. Results show that the highest yield (12%) was obtained at the highest liquid-to-solid ratio (4 mL g⁻¹) and temperature (60 °C).

The maximum yield obtained by ultrasound-assisted extraction was similar to the yield reported by Cholakov et al. (2013), but slightly lower than the yield reported by Al-Hamamre et al. (2012). The results show that the ultrasound-assisted extraction was able to extract the oil from SCG under milder conditions and faster than other methods (Al-Hamamre et al., 2012; Cholakov et al., 2013). The small differences in yield may also be caused by different brewing methods of the fresh ground coffee beans (Gross et al., 1997) and by different types of fresh coffee, coffee arabica and coffee robusta for example, which have different lipids content (Al-Hamamre et al., 2012; Oliveira et al., 2008).

The yields obtained under the conditions of the central point of the factorial design were relatively close evidencing good reproduction of the experiments and the consistency of the method. The use of hexane as solvent showed to be satisfactory since it was able to extract the oil. The non-polar solvents carry no or only low charges and the extraction process is based on Van der Waals forces and thus they were able to penetrate into the matrix of the ground coffee.

The liquid-to-solid ratio (solvent/SCG), temperature and their interaction had positive effects over the yield of SCG oil (Table 2). However, just the solvent to SCG ratio was statistically significant at the confidence level of 95%. This fact can be explained by an increase in the mass transfer, where the oil can diffuse from a more concentrated region (oil sludge) to a less concentrated (solvent) region. The use of ultrasound causes an increase in the effective diffusivity of the oil in the ground coffee toward the solvent and it is probably due to the sponge effect caused by cavitation and breakdown of the tissue structure of the ground coffee (Abdullah and Koc, 2013). Sonication also creates micro-explosions that enhance the penetration of the solvent into the organic matrix (Rodrigues et al., 2009).

The temperature had a lower influence on the yield of oil when compared to the solvent to spent coffee ground. Although an increase in yield was observed with the increase in temperature, this increase rate tends to diminish at higher temperatures because the effect of ultrasound decreases as temperature increases. The extraction with ultrasound may be advantageous due to low energy consumption when compared to heating method.

The SCG oil presented an acid value of 16.59 mg KOH/g oil and a density of 0.89 kg m⁻³. The oil was composed of 40.2% linoleic acid (C18:2), 35.9% palmitic acid (C16:0), 10.7% oleic acid (C18:1), 7.5% stearic acid (C18:0), 2.6% arachidonic acid (C20:4), 0.7% behenic acid (C22:0), 0.4% linolenic acid (C18:3) and 2.0% other fatty acids. The molar mass of the oil was 862.8 g mol⁻¹ and was calculated based on its composition. The oil presents high amounts of palmitic and linoleic acids; and a high amount of unsaturated fatty acids (>50%), which are more susceptible to oxidation.

3.2. Biodiesel production

The yield of oil into biodiesel was 97% under the conditions applied herein, which were based on prior optimization works of

Table 2
Analysis of perturbation of factors on the yield of oil obtained by ultrasound-assisted extraction. Variables written in bold are significant at a 95% level of confidence.

Variable	Effects	Standard deviation	t-Student	p
Mean	6.6428	0.2212	30.0254	0.0011
Solvent to SCG ratio	7.8350	0.5853	13.3852	0.0055
Temperature	1.7550	0.5853	2.9982	0.0955
Ratio × temperature	1.2350	0.5853	2.1098	0.1693

our group (Santos et al., 2010; Lima et al., 2012). This yield ensures that the biodiesel will have more than 96–96.5% of ester content, which is the minimum ester content required by regulating agencies in Europe, USA and Brazil (that follows EN 14214, ASTM D6751 and similar standards) for commercial biodiesel. Thus, SCG oil can be considered a viable raw material for the production of biodiesel.

The fatty acid composition profile of the biodiesel was equal to the composition of its oil source. The composition of the biodiesel produced from SCG oil is close to the composition profile of soybean oil and corn oil, both used to make biodiesel.

The high acid value of the SCG oil do not allow direct transesterification of the oil, which would produce high amounts of soap and reduce the overall conversion into biodiesel. Thus, the oil can be esterified and then transesterified, or it can go through saponification followed by acid hydrolysis and esterification. In this work, the second route was chosen because fast and efficient saponification and esterification can be achieved by ultrasound application. The neutralization step that was carried out in the experiments after acid hydrolysis can be dismissed in an industrial process and it was only done in the experiments to ensure a precise concentration of sulfuric acid during the esterification step.

3.3. Ethanol production

3.3.1. Hydrolysis of the oil-free spent coffee grounds

The results for the hydrolysis of the oil-free spent coffee grounds carried out at different sulfuric acid concentration (0.0 mol L^{-1} , 0.4 mol L^{-1} and 0.8 mol L^{-1}), using a constant solid concentration of 20% in the slurry, are shown in Table 3. A high sugar concentration ($>37 \text{ g L}^{-1}$) was obtained in the hydrolysate compared to the control experiment (without addition of sulfuric acid).

The ANOVA results showed that the concentrations and yields of glucose (38 g L^{-1} and $190 \text{ mg g}_{\text{SCG-OF}}^{-1}$, respectively) were not significantly influenced by the use of sulfuric acid at concentrations from 0.4 mol L^{-1} and 0.8 mol L^{-1} . These results were similar to the trend observed when using other raw materials (Rocha et al., 2014; Saha et al., 2005). Saha et al. (2005) obtained total glucose yield of $189 \text{ mg g}_{\text{RICE BRAN}}^{-1}$ when $0.2 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ was used in 15 % of rice bran. Rocha et al. (2014) obtained its best condition applying a dilute acid pretreatment in the hydrolysis of cashew apple bagasse: $0.6 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ for 15 min at $121 \text{ }^\circ\text{C}$ with 30% of solids.

The highest concentration of xyloarabin ($4.63 \pm 0.3 \text{ g L}^{-1}$) was obtained when 0.4 mol L^{-1} of sulfuric acid was used in the pretreatment, yielding $23.2 \pm 1.5 \text{ mg g}_{\text{SCG}}^{-1}$. Higher concentrations of H_2SO_4 reduced the concentration of xyloarabin, which may be caused by the breakdown of these sugars forming lactic acid ($1.94 \pm 0.1 \text{ g L}^{-1}$) and acetic acid ($1.51 \pm 0.5 \text{ g L}^{-1}$). The ANOVA analysis showed that the xyloarabin concentration was significantly influenced by the H_2SO_4 concentration. A similar behavior was observed with the conversion of xyloarabin. Analysis using Tukey test showed that the xyloarabin concentrations were significantly

different when the hydrolysis was conducted using 0.4 mol L^{-1} and $0.8 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$.

Compounds that can act as potential inhibitors for the fermentation, such as lactic and acetic acids, can be originated from lignocellulosic materials at high temperatures and acid conditions (Alvira et al., 2010; Saha et al., 2005). No detectable quantities of furfural or hydroxymethyl furfural were detected in the hydrolysate (concentration $<0.001\%$). The highest concentration of lactic and acetic acids was obtained when the oil-free SCG was hydrolyzed using $0.8 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, which might have been caused by degradation of sugars under these conditions. To evaluate the influence of acetic and lactic acids in the metabolism of the yeast to produce ethanol, both hydrolysates (0.4 and 0.8) mol L^{-1} were used as culture media in the fermentations.

3.3.2. Ethanol production

Fig. 1 shows the kinetics for glucose and xylose consumption and for ethanol production at $30 \text{ }^\circ\text{C}$ and 150 rpm during the fermentation of the hydrolysates of the oil-free SCG obtained using the 0.4 mol L^{-1} and 0.8 mol L^{-1} solutions of H_2SO_4 .

Nearly all the glucose present in the medium was consumed during the fermentation of the hydrolysate obtained with $0.4 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution, while the concentration of xyloarabin remained constant. There was no change in the pH, which remained between 4.5 and 5.0 (data not shown). Under the conditions studied in this work, $18.9 \pm 0.3 \text{ g L}^{-1}$ of ethanol was obtained after 10 h of fermentation, with an ethanol yield of $0.50 \text{ g}_{\text{ethanol}} \text{ g}_{\text{glucose}}^{-1}$ and a productivity of $1.90 \text{ g L}^{-1} \text{ h}^{-1}$.

Similar behavior was observed during the fermentation of the hydrolysate obtained with the $0.8 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution. Nearly all glucose was consumed; remaining only 2 g L^{-1} of glucose from the hydrolysate, and the xyloarabin concentration also remained constant during the process. No change was observed in the pH, which remained between 4.5 and 5.0 (data not shown). The ethanol concentration obtained after 10 h of fermentation was at $17.2 \pm 0.3 \text{ g L}^{-1}$, with a yield into ethanol of $0.47 \text{ g}_{\text{ethanol}} \text{ g}_{\text{glucose}}^{-1}$ and a productivity of $1.72 \text{ g L}^{-1} \text{ h}^{-1}$. High acetic acid concentrations did not influence the production of ethanol. The presence of components, such as acetic acid, in the medium usually influences the process kinetics and economics, but in this study, the nutrients present in the hydrolysates were not affected by inhibitory compounds and lead to satisfactory cell growth and ethanol production.

The ethanol yield obtained herein was similar to yield reported by Kwon et al. (2013), without having to carry out an enzyme hydrolysis of the spent coffee grounds as done by Kwon et al. (2013). The processing time was also shorter than the time reported by Kwon et al. (2013). Ethanol production using spent coffee grounds as feedstock was similar to the production obtained using others agro-industrial wastes. Yu and Zhang (2003) obtained an ethanol concentration of $15.1 \pm 1.07 \text{ g L}^{-1}$ for the fermentation of pyrolyzed-hydrolyzed cotton residue, while Rocha et al. (2014)

Table 3
Compositional analysis of hydrolysates obtained after acid hydrolysis of oil-free spent coffee grounds carried out at $121 \text{ }^\circ\text{C}$ for 15 min using 20% of SCG. Values in parenthesis correspond to the yield based on the mass of oil-free SCG (mg g^{-1}). Different lower-case letters indicate statistical difference at $\alpha = 0.05$ level in each column.

Sample	Glucose (g L^{-1})	Xyloarabin (g L^{-1})	Lactic acid (g L^{-1})	Acetic acid (g L^{-1})
Hydrolysis with $0.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$	1.5 ± 0.2^a (7.5 ± 1.0)	0.3 ± 0.1^a (1.5 ± 0.5)	ND	ND
Hydrolysis with $0.4 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$	38.55 ± 0.1^b (192.75 ± 0.5)	4.63 ± 0.3^b (23.15 ± 1.5)	2.12 ± 0.1^a (10.60 ± 0.5)	0.79 ± 0.0^a (3.95 ± 0.0)
Hydrolysis with $0.8 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$	37.73 ± 1.1^b (188.65 ± 5.5)	4.08 ± 0.1^c (20.40 ± 0.5)	1.94 ± 0.1^a (9.70 ± 0.5)	1.51 ± 0.5^b (7.55 ± 0.5)

ND – not detected.

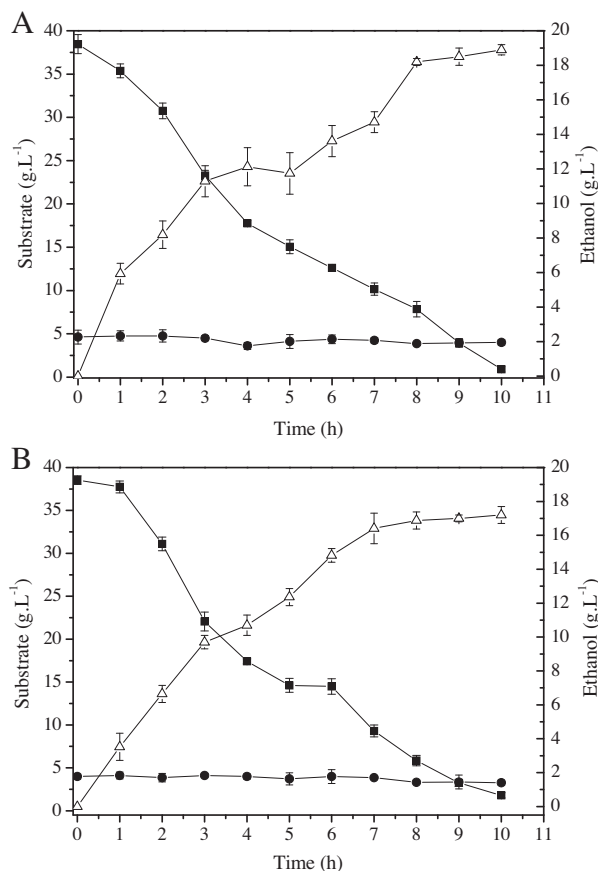


Fig. 1. Ethanol production and sugars consumption by *S. cerevisiae* at 30 °C and 150 rpm using, as culture media, the hydrolysates from oil-free spent coffee grounds at different H₂SO₄ concentrations: (■) glucose concentration (g L⁻¹); (●) xylarabin concentration (g L⁻¹); (Δ) ethanol concentration (g L⁻¹). (A) Hydrolysate obtained with 0.4 mol L⁻¹ H₂SO₄ and (B) hydrolysate obtained with 0.8 mol L⁻¹ H₂SO₄.

has obtained 10.0 ± 0.1 g L⁻¹ of ethanol in the fermentation of hydrolyzed cashew apple bagasse.

The results show that the fermentation of sugars liquors obtained after hydrolysis of lignocellulosic materials was the critical stage. The fermentative assay that was carried out has obtained high ethanol yield in a short fermentation period (8–10 h).

3.4. Overall mass balance and energy considerations

A mass balance of the process, considering as basis 100 g spent coffee grounds, was carried out and a schematic diagram is shown in Fig. 2. The ultrasound-assisted extraction of the oil from spent coffee ground yielded 12% (13.5 mL) of oil under optimal conditions. The oil obtained from the spent coffee ground was converted into fatty acids and then into biodiesel through ultrasound-assisted esterification. The yield into biodiesel was 97% (13.1 mL biodiesel).

The mass of the recovered oil-free spent coffee ground corresponded to 88% of the initial mass and was subjected to hydrolysis aiming ethanol production. The oil-free spent coffee ground at a solid loading of 20% was hydrolyzed under operating conditions (0.4 mol L⁻¹ H₂SO₄, 121 °C, 15 min) were a maximum sugar recovery was obtained. The hydrolysate was separated from the remaining solid fraction prior to ethanol production. The sugar yield was equivalent to 17 g of glucose per 100 g of initial material. Finally, the yield of ethanol was 0.5 g g⁻¹ (8.3 g, corresponding to

10.6 mL), which represents approximately 99% of the yield that could be theoretically obtained. According to Fig. 2, the spent coffee grounds can be a potential source for the production of biodiesel and ethanol.

The energy return on energy invested (EROI) can be defined as the ratio between energy obtained and energy consumed during production. As the objective of any fuel is to provide energy, the EROI ratio is a concept very useful for evaluating the fuel obtaining process efficiency (Esteban et al., 2011). In a simplified form, the EROI of a given process can be calculated based on the heat of combustion (ΔH_C) of the reactants and the products, the required thermal energy used in the process, the required mechanical energy used in the process, and the required ultrasound energy used in the process (Eq. (1)).

$$\text{EROI} = \frac{\text{energy gained}}{\text{energy invested}} = \frac{\Delta H_C(\text{products}) - \Delta H_C(\text{reactants})}{E_{\text{thermal}} + E_{\text{mechanical}} + E_{\text{ultrasound}}} \quad (1)$$

The data used to calculate thermal requirements and the heat of combustion of oil and methyl esters was obtained from Osmont et al. (2007) and these data were calculated as a weight average of the different FFAs and esters chains that comprises SCG oil and the produced methyl esters. The data used in EROI calculations are summarized in Table 4.

SCG oil have high heat of combustion ($\Delta H_C = -32,248 \text{ kJ mol}^{-1}$) and its respective methyl esters have also high heat of combustion ($\Delta H_C = -11,170 \text{ kJ mol}^{-1}$) and are comparable to biodiesels produced from soybean. The esterification of SCG FFAs with methanol ($\Delta H_C = -239.5 \text{ kJ mol}^{-1}$) will add to the products 2216 kJ mol⁻¹ in heat of combustion (energy gained).

Although the experiments carried out herein used a low power ultrasonic bath, which would probably be used in large scale processing, the amount of energy invested in the reaction was 1025 kJ mol⁻¹ under optimal conditions, considering the both heating and ultrasonic application. Thus, the amount of energy invested was lower than the energy gained during the reaction. The EROI for the process was 2.1, so the process for biodiesel production could be considered viable from a heat of combustion point of view. The EROI of the process drops to 0.3 when the energy needed to extract the oil is considered, caused by the high demand

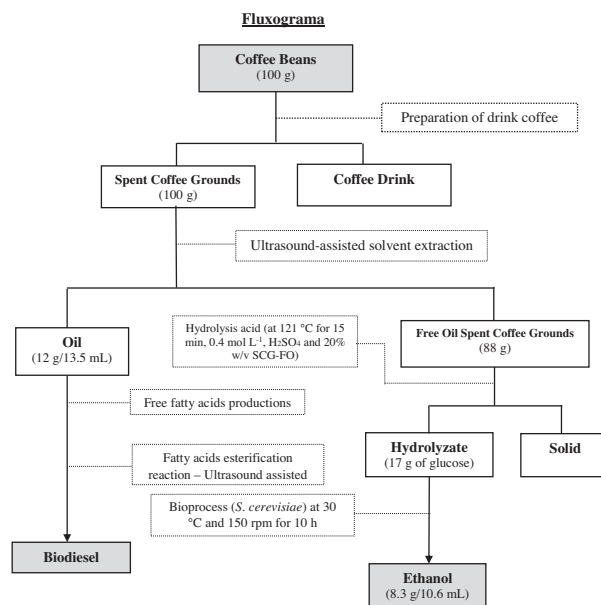


Fig. 2. Schematic diagram for the mass balance of biodiesel and ethanol production from spent coffee grounds.

Table 4

Data used in energy return on energy invested (EROI) calculation for methyl ester production and ethanol production from spent coffee grounds.

SCG oil density	862 g L ⁻¹
SCG oil heat capacity	0.32 kJ mol ⁻¹ K ⁻¹
SCG oil heat of combustion	-32,248 kJ mol ⁻¹
Methanol density	789 g L ⁻¹
Methanol heat capacity	0.112 kJ mol ⁻¹ K ⁻¹
Methanol heat of combustion	-240 kJ mol ⁻¹
Methyl ester density	870 g L ⁻¹
Methyl ester heat capacity	0.42 kJ mol ⁻¹ K ⁻¹
Methyl ester heat of combustion	-11,170 kJ mol ⁻¹
Ethanol density	789 g L ⁻¹
Ethanol heat capacity	0.112 kJ mol ⁻¹ K ⁻¹
Ethanol heat of combustion	-1367 kJ mol ⁻¹
Ultrasound power for the extraction	500 W
Ultrasound power for the reaction	100 W
Mechanical stirrer power	15 W

for energy by the extraction process. Under this condition, the use of SCG oil would not be energetically viable for biodiesel production, but could be economically viable for other applications such as pharmaceuticals.

Ethanol has a heat of combustion (ΔH_c) of $-1368 \text{ kJ mol}^{-1}$. The production of ethanol requires an energy intensive step (hydrolysis), which demands approximately 1150 kJ mol^{-1} of ethanol mainly due to the need of vaporization of water. The fermentation step is not energy intensive but that has a long processing time (10 h) demanding approximately 500 kJ mol^{-1} of ethanol, used mainly for agitation of the reaction mixture.

Under this condition, the production of ethanol is energetically viable only if the energy required in the hydrolysis step is recovered and used elsewhere in the process. Most of the energy required by the hydrolysis step can be recovered because it consists of internal energy. Energy integration in a biorefinery, using pinch technology, can reduce the need of external source of energy and increase the EROI of both ethanol and biodiesel production to viable levels.

4. Conclusions

This study demonstrated that spent coffee grounds can be used as raw material in a biorefinery to produce both biodiesel and ethanol. Oil from spent coffee grounds can be extracted ultrasound-assisted extraction yielding 12% of oil consisting mainly of palmitic and linoleic acids, and shows potential application for biodiesel production. The oil-free spent coffee grounds had potential application to produce carbohydrates for ethanol production by fermentation. The process resulted in a yield into ethanol of $0.50 \text{ g}_{\text{ethanol}} \text{ g}_{\text{glucose}}^{-1}$ and a productivity of $1.9 \text{ g L}^{-1} \text{ h}^{-1}$.

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